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INTERIM REPORT

INVESTIGATION OF THE AUTOXIDATION
OF PETROLEUM FUELS

BY

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INVESTIGATION OF THE AUTOXIDATION OF PETROLEUM FUELS

BY

MAURICE E. LE PERA

JUNE 1966

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U.S. ARMY COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND

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ABSTRACT

The deterioration of petroleum fuels was studied by investigation of their autoxidation susceptibilities. Federal and Military Specification fuels and commercial gasolines were subjected to a six-week accelerated aging test with analyses for generated hydroperoxides determined at weekly intervals. The resulting peroxide-time curves revealed autoxidation tendencies to vary considerably. Under the conditions of this aging technique, there is evidence that the bulk storage supply of combat gasoline (MIL-G-3056B) at Aberdeen Proving Ground is experiencing a gradual depletion of antioxidant quality.

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1. INTRODUCTION

The major problems arising from the bulk storage of petroleum fuels are primarily the results of fuel instability. Fuel stability may be defined as the property of resistance to significant material change or to deterioration (1). Deterioration in petroleum fuels occurs by autoxidation (2), which initially may be described as the self-oxidation of organic materials under mild conditions (ambient temperature and atmospheric pressure). The tendency of a specific petroleum fuel to autoxidize is directly related to its hydrocarbon type, with the order of decreasing reactivity towards autoxidation generally regarded as diolefins, aromatic olefins, aliphatic olefins, alkyl aromatics, naphthenes, and paraffins (3). Autoxidation is defined as a free radical-initiated, chain reaction decomposition with the process occurring by a two step mechanism (4,5,6,13). Initially, hydrocarbons react slowly with atmospheric oxygen to give alkyl or aryl hydroperoxides, the first products of molecular oxidation (5,7,9,11). Then decomposition of the "relatively unstable" hydroperoxides produces free radical chain carriers, which react to form secondary oxidation products (4) (i.e. aldehydes, ketones, hemiacetals, esters, etc.). The latter are the monomer ingredients for the polymeric complexes eventually forming "insoluble gums". The rate of autoxidation is dependent on the rate of disassociation of the hydroperoxides (9). The latter is dependent on the presence of trace amounts (P.P.B.) of heavy metals such as copper and cobalt (10).

It has been reported that the presence of hydroperoxide species in petroleum fuels has resulted in the following:

(1). Hydroperoxides decrease the octane rating of a gasoline, an increase in one hydroperoxide number causing a unit decrease in Motor Octane Number (18); (2). hydroperoxide - containing distillate fuels have invariably been shown to produce severe tube deposits in the ASTM D-1660 Thermal Stability Test for Aviation Fuels (4); and (3). unsatisfactory engine cleanliness has been experienced where thermal and catalytically cracked gasolines showed hydroperoxide numbers as low as 0.40 milliequivalents of active oxygen per liter (21). However, the latter statement should not be utilized as the maximum allowable level for evaluating fuels, since the correlation between sensitivity and response of different gasoline types has not yet been definitely established.

Since it has been shown that the first step in the autoxidation of hydrocarbons is the formation of hydroperoxides, the analysis for these compounds in petroleum fuels with respect to exposure time should give a meaningful evaluation of storage stability. Furthermore, it has been reported that the hydroperoxide concentration is useful for rate comparison during initial stages of autoxidation (12). The determination of autoxidation products other than peroxides is very difficult

(14) due to the complexity of compound types.

This interim report, a preliminary study of fuel stability, covers the initial evaluation of petroleum fuel autoxidation using hydroperoxide number-time curves to measure oxidative deterioration at 150°F. In addition, the use of current standard procedures to assess this deterioration is discussed.

II. DETAILS OF TEST

A. Peroxide Determination

Organic peroxides are determined by their oxidative properties. Iodometric methods, as well as ferrous ion methods, have been used for the determination of peroxides in oxidized organic materials. The most common criticism of the former has been that iodine liberated in the reaction disappears by addition to the olefinic bond in unsaturated hydrocarbons, resulting in excessively high values (15, 25). The ferrous method has been shown to be subject to error, and cannot be relied on for accuracy (16). The arsenious oxide method for the analysis of peroxides in petroleum products (17) was selected due to its increased sensitivity and lack of olefinic interference (26). In addition, the accuracy of the arsenious oxide method in petroleum product applications has been confirmed by recent work (18).

B. Accelerated Exposure

Using conventional storage exposure where ambient temperature is not subject to appreciable fluctuation, the time required to autoxidize a petroleum fuel is much too great for laboratory procedures. This laboratory has worked extensively with evaluating the compatibility of fuel resistant coatings in petroleum fuel environments and has obtained satisfactory correlation with field storage data using an accelerated 150°F. test of sealed fuel containers. This exposure temperature was selected for the autoxidation study. Representative petroleum fuels were exposed at 150°F. for a total of 6 weeks. A sample was removed each week and its hydroperoxide number (17) representing the number of milliequivalents of active oxygen per liter was determined the same day to prevent additional shelf aging. Six individual bottles were used for each fuel type to prevent any discrepancies arising from non-uniformities of fuel-vapor volumes resulting from sampling. The storage containers (sample bottles) were amber 500 ml., narrow-mouth, screw-cap bottles, which were acid washed, rinsed twice with distilled water, and oven dried, to minimize solvent contamination prior to use. The screw caps were fitted with gaskets cut from 1/16" Viton AHV elastomer sheet stock. Before filling the sample bottle, the fuel was chilled at 50°F. to prevent loss of the more volatile hydrocarbon ingredients. After filling the sample bottle

with 200 ml. of fuel, the vapor area above the fuel was gently purged with oxygen for 30 seconds before sealing to insure maximum availability of oxygen for the six-weeks storage period. The 300 ml. (approximately 25 milliequivalents at ambient temperature) of oxygen in the storage bottle provides a sufficient excess, since the maximum pick up in these studies (obtained only once) was a hydroperoxide number of 70 milliequivalents per liter (corresponding to only 21 milliequivalents consumed per 300 ml. sample).

III. RESULTS AND DISCUSSIONS

A. Military & Federal Specification Automotive & Aircraft Fuels.

The effects of accelerated autoxidation, exposure at 150°F. in an oxygen atmosphere, on different military and federal specification fuels was measured by hydroperoxide number-time curves are illustrated in Figure 1 (Appendix B). The sample demonstrating the maximum rate of autoxidation was the Federal Specification VV-G-109 Gasoline, Unleaded. This fuel, being lead-free, contains additions of aromatic, isoparaffinic, and olefinic hydrocarbons, high in octane number, in order that the finished fuel blend satisfy the current octane number requirements normally attained by the addition of lead alkyl compounds. The reason for the extremely rapid uptake of oxygen, chemically reacting to form hydroperoxides, may be the appreciable contents of olefins and alkyl aromatic hydrocarbons which are particularly susceptible to autoxidation.

The reason for the VV-G-76 Gasoline, Regular Grade, apparently exhibiting a greater resistance towards autoxidation than MIL-G-3056 Gasoline, Combat, which is blended to possess maximum oxidation resistance for long storage periods, is the "fresh" condition of VV-G-76 due to bi-monthly delivery from local refineries. As was anticipated because of its primarily isoparaffinic hydrocarbon composition, the MIL-G-5572C Gasoline, Aviation, was very resistant to autoxidation as evidenced by the relatively slow increase in hydroperoxide concentration. The rather limited response of the MIL-J-5624 F Jet Fuel, Grade JP-4 and MIL-F-45121B Fuel, Compression-Ignition and Turbine Engine to hydroperoxide formation is due to the presence of disulfide compounds which exist in trace quantities. It has been reported that disulfides either react directly with oxygen preventing hydroperoxide formation, or react so rapidly with any hydroperoxides that may be found that the former cannot be detected (19).

B. Commercial Motor Gasolines.

The effects of the accelerated autoxidation on commercial regular and premium grade gasolines are shown in Figure 2 (Appendix B). It is to be noted that the fuels selected for this investigation were obtained from service stations having rapid turnover of their products,

thereby minimizing the preliminary pre-oxidation which may occur in their storage tanks. The gasoline demonstrating the maximum rate of autoxidation was Premium Brand D, while the maximum resistance to autoxidation or minimum rate of autoxidation was shown by Premium Brand B. The other four gasolines, Regular Brand A, Premium Brand A, Regular Brand B, & Premium Brand C, appear to be similar in their tendencies to autoxidize; and their curves lie approximately midway between the maximum (Premium Brand D) and minimum (Premium Brand B) rates of autoxidation.

A comparison of the autoxidation tendencies of these commercial fuels (Figure 2) and the previously discussed military and federal specification fuels (Figure 1) indicates distinct similarities. All of the fuels fall into one of three groups, each group demonstrating a different degree of autoxidation. The first group, including Premium Brand D and VV-G-109, is characterized by an initial, extremely rapid increase in autoxidation, with the maximum attained after approximately one week of aging at 150°F., followed by almost as sharp a decrease in the rate of autoxidation. This type of peroxide-time curve is indicative of fuels expected to have poor storage stability. Although these fuels exhibit extremely rapid peroxide-uptake reactions in the 150°F. accelerated aging test, their autoxidation rates would be less pronounced at ambient temperatures. They would, however, have a marked tendency to oxidize.

It would seem that the initial steep positive slope of the hydroperoxide number-time curve represents a primary oxidation stage in which trace amounts of free radicals, formed by the action of an initiator, abstracting hydrogen from olefinic or tertiary carbon configurations, with hydroperoxides formed at the site of abstraction. The hydroperoxides eventually being to dissociate (22) because of their instability, thus initiating a secondary oxidation stage, which is characterized by a greater peroxide dissociation rate than generation rate. This is reflected in the sharp decrease of the hydroperoxide number-time curve. The second group of fuels has curves showing very small rates of autoxidation, Fuels MIL-F-45121B and MIL-J-5624F are characteristic of this group. After 6 weeks exposure at 150°F., their hydroperoxide number is low and has shown no significant increase, indicating good storage stability. A third group of fuels, exemplified by VV-G-76 and MIL-G-5572C, have hydroperoxide number-curves which indicate a relatively slow increase in peroxide concentration, with neither fuel having attained a maximum rate of autoxidation after 6 weeks exposure at 150°F.

C. Repeatability of Autoxidation Rates.

The determination of autoxidation rates was accomplished by the analysis of the exposed fuel samples at different time intervals. The repeatability of test results was not determined because of limited

exposed fuel sample for analysis (200 ml. total sample), varying sample size requirements (See Table I, Appendix A) and time required for analysis. However, a measure of their precision was obtained by evaluating two identical samples of MIL-G-3056B simultaneously. The results (Table II, Appendix A) show good repeatability for the technique. In addition, a sample of VV-G-76, obtained two months after the initial VV-G-76 sample, was evaluated to confirm the reproducibility of the initial test results. A comparison of the two sets of obtained results (Table II, Appendix A) indicate the validity of this technique with respect to test repeatability.

D. Depletion of Antioxidant Quality of MIL-G-3056B in Bulk Storage.

Figure 3 (Appendix B) is a graphical representation of the autoxidation sustained by MIL-G-3056B in bulk storage facilities (Aberdeen Proving Ground) during a 17 week interval, as illustrated by hydroperoxide number-time curves. Samples were removed from the bulk storage tank at the start of the test, after 6 weeks and after 17 weeks, and then individually evaluated by the accelerated autoxidation technique. Using the sample removed initially, 30 December 1964, as a basis for comparison, it is evident that the longer the fuel remains in bulk storage, the greater the susceptibility towards hydroperoxide formation at 150°F. in presence of oxygen. This increasing tendency towards autoxidation (under these conditions) can be attributed to the depletion of antioxidant quality. This particular quantity of MIL-G-3056B was delivered to Aberdeen Proving Ground in August 1964. To maintain quality assurance, personnel from Supply Division periodically withdraw samples from the bulk storage supply and send these samples to Schenectady Army Depot, Petroleum Division, for complete specification analysis. The tabulation of test results, directly related to stability, which was obtained from Supply (Table III, Appendix A) does not reveal any significant decrease in storage stability or deterioration.

Concurrent with this test series, additional tests were conducted to evaluate this accelerated aging of the MIL-G-3056 fuel. It has been reported that the filtration of fuels through carbon black removes the precursors of induction system deposits (20). A sample of MIL-G-3056 was filtered through carbon black and the filtered fuel evaluated by the accelerated autoxidation technique. In addition, a sample of the MIL-G-3056 not filtered through the carbon black was treated as prescribed in paragraph 6.1 of Federal Specification VV-G-800 Gasoline, Gum Preventative. This involves the addition of a prescribed amount of the following composition: 41 grams of alkylated phenol antioxidant and 10 grams metal deactivator dissolved in 1 gallon of toluene. It should be noted that although this gum preventative is not intended for use with MIL-G-3056, it was employed for screening purposes due to the non-availability of commercial antioxidants. Figure 4 (Appendix B) illustrates the beneficial effects of these two pretreatments. From the limited test data, there appears to be a correlation between

autoxidation susceptibility and induction system deposit tendency.

E. Comparison of the Autoxidation Results with Standard ASTM Stability Procedures.

The fuels in this investigation were concurrently evaluated using standard procedures for determining fuel instability given in ASTM Standards on Petroleum Products (23) (Table IV, Appendix A). In ASTM D-525, Oxidation Stability of Gasoline, all the gasolines both military and commercial, exhibited satisfactory induction periods which are indicative of gasolines possessing oxidation resistance. However, the results of this investigation have shown that VV-G-109 and Premium Brand D, while giving the highest induction periods of all automotive gasolines, had relatively no resistance towards autoxidation under the conditions of the accelerated 150°F. autoxidation test. It should be noted that the test conditions for ASTM D 525 are 212°F. at 100 psig oxygen whereas the conditions of the technique developed for this investigation are 150°F. at 0 psig oxygen.

The ASTM D-381 Test for Existent Gum measures the tendency of a petroleum fuel to form insoluble "gum" deposits, this tendency being related directly to its oxidation resistance. The obtained "gum" values (Table IV, Appendix B) for the military and commercial fuels did not differ appreciably. However, the two fuels, VV-G-109 and Premium D, which exhibited very poor autoxidation resistance, had very low "gum" values. The significant disagreement of test data between ASTM procedures and the autoxidation evaluations indicate the varying insensitivity of current methods to measure actual fuel deterioration.

IV. CONCLUSION

The results of this investigation illustrate the need for a more precise manner of determining fuel instability. The technique developed for this investigation permits an accurate determination of the initial autoxidation rate which can be utilized to anticipate the degree of fuel stability. However, the time required to obtain results is somewhat lengthy for an accelerated bench scale technique. The results have shown that the response level of blended fuels towards autoxidation is sufficient to give a measurable differentiation.

V. RECOMMENDATIONS

It is recommended that this work be continued to develop a laboratory, bench-scale test for determining the rates of autoxidation directly.

This requires the application of a Walberg-Respirometer apparatus to measure the amount of oxygen absorption at various temperature levels, eliminating the exposure or storage periods. Recent work (24) employing

a direct-reading oxygen absorption device (a Walberg Respirometer) has been conducted whereby the oxidation stability of lubricating oils were determined. Concurrent with the proposed test development, a second phase would be initiated to determine the deposit formation of motor fuels utilizing a developed bench-scale procedure (20). Ultimately, it is desired to establish a correlation between the initial rate of autoxidation and the deposit tendency of petroleum fuel.

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30. Military Specification MIL-J-5624F, Jet Fuel, Grade JP 4.
31. Federal Specification VV-G-76, Gasoline, Regular Grade.

32. Federal Specification VV-G-109, Gasoline, Unleaded.

33. Federal Specification VV-G-800, Gum Preservative, Gasoline.

APPENDIX A

TABLE I

SAMPLE SIZE REQUIREMENT FOR HYDROPEROXIDE NO* ANALYSIS

<u>Anticipated Hydroperoxide No.</u>	<u>Sample Size Required, ml.</u>
0 to 1	100.0
1 to 5	50.0
5 to 10	25.0
10 to 50	10.0
50 to 100	5.0
100 to 1000	0.50

* Millequivalents of active oxygen per liter

TABLE II

REPEATABILITY OF AUTOXIDATION RATES

A. For Identical MIL-G-3056 Samples -

<u>Hydroperoxide No.</u>		<u>Weeks Exposed</u>
<u>Sample A</u>	<u>Sample B</u>	<u>At 150°F.</u>
0.30	0.25	1
0.75	0.71	2
4.31	4.40	3
44.56	43.47	4
31.60	30.95	5
18.60	18.00	6

B. For Different VV-G-76 Samples -

<u>Hydroperoxide No.</u>		<u>Weeks Exposed</u>
<u>Sample C*</u>	<u>Sample D**</u>	<u>At 150°F.</u>
0.35	0.15	1
0.73	0.46	2
1.05	0.92	3
2.44	1.86	4
2.86	3.87	5
10.19	15.10	6

* Initial sample of VV-G-76

** Sample of VV-G-76 obtained one month later

TABLE III

MIL-G-3056 QUALITY ASSURANCE INSPECTION RESULTS

Date Sample Withdrawn	ASTM-D381, Existent Gum, mg/100ml*	ASTM-D525, Oxidation Stability, Min.
August 1964	0.6	720
October 1964	1.4	480 +
January 1965	1.2	480 +
March 1965	3.4	480 +
July 1965	1.9	480 +

*Figures listed are average of three determinations.

TABLE IV

Fuel Evaluated	DETERMINATION OF FUEL STABILITY USING CURRENT ASTM PROCEDURES		
	(Oxidation Stability)		
	ASTM D-381* Existent Gum, mg/100ml.	ASTM D-525** Induction Period, min.	ASTM D-873*** Potential Gum, mg/100ml.
MIL-G-5572C, Aviation Gasoline	1.4	1320	--
MIL-G-30568, Combat Gasoline	1.2	200	--
VV-G-76, Regular Gasoline	1.0	600	--
VV-G-109 Unleaded Gasoline	1.8	1260	--
Regular Brand A	4.2	480	--
Premium Brand A	0.8	300	--
Regular Brand B	0.8	1260	--
Premium Brand B	1.0	600	--
Premium Brand C	1.6	870	--
Premium Brand D	4.0	360	--
MIL-F-45121B, C.I.T.E. Fuel	0.8	--	16.6
MIL-J-5624F JP-4 Fuel	0	--	14.0

APPENDIX B

FIGURE 1: AUTOXIDATION OF SPECIFICATION FUELS

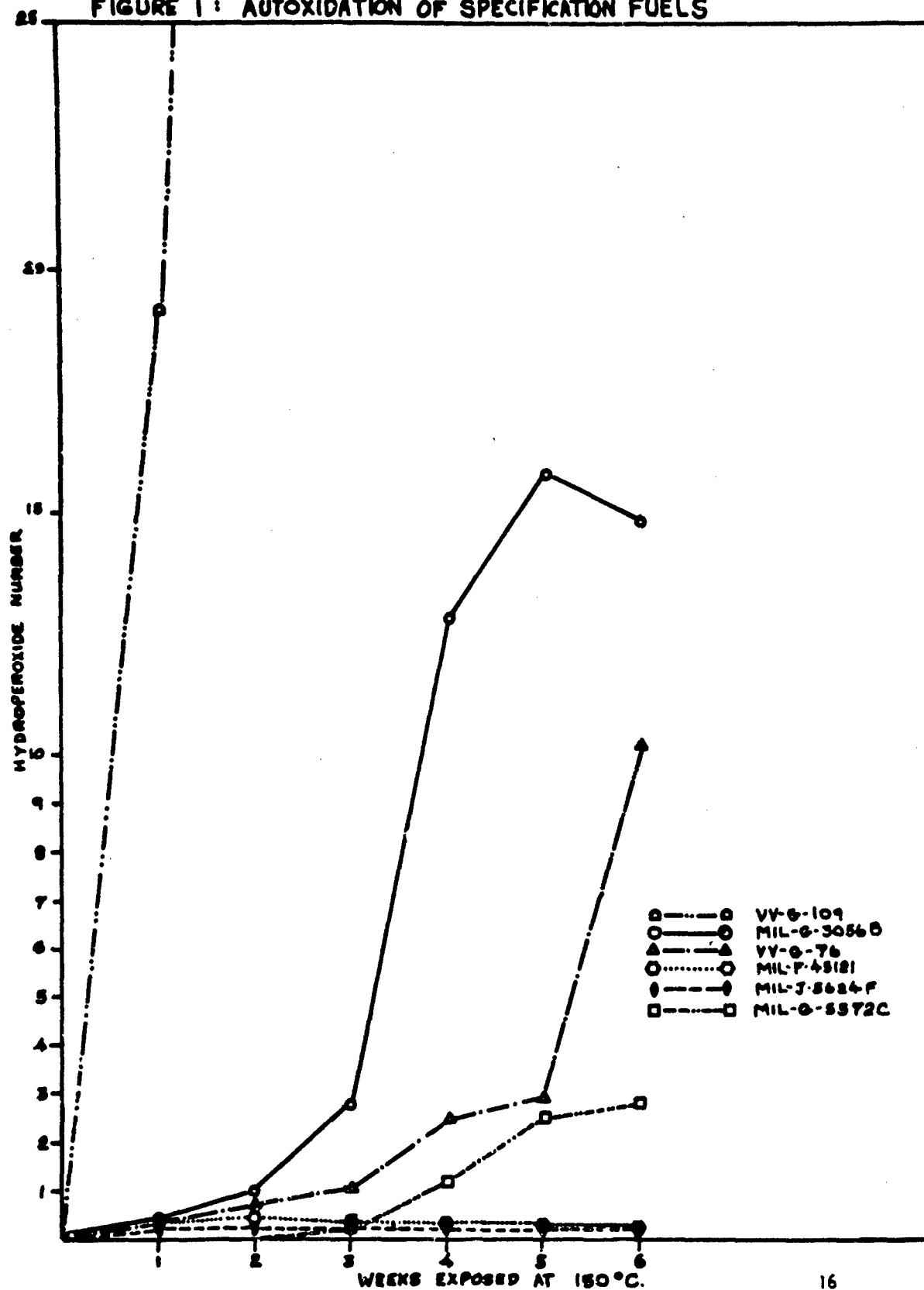


FIGURE 2: AUTOXIDATION OF COMMERCIAL GASOLINES

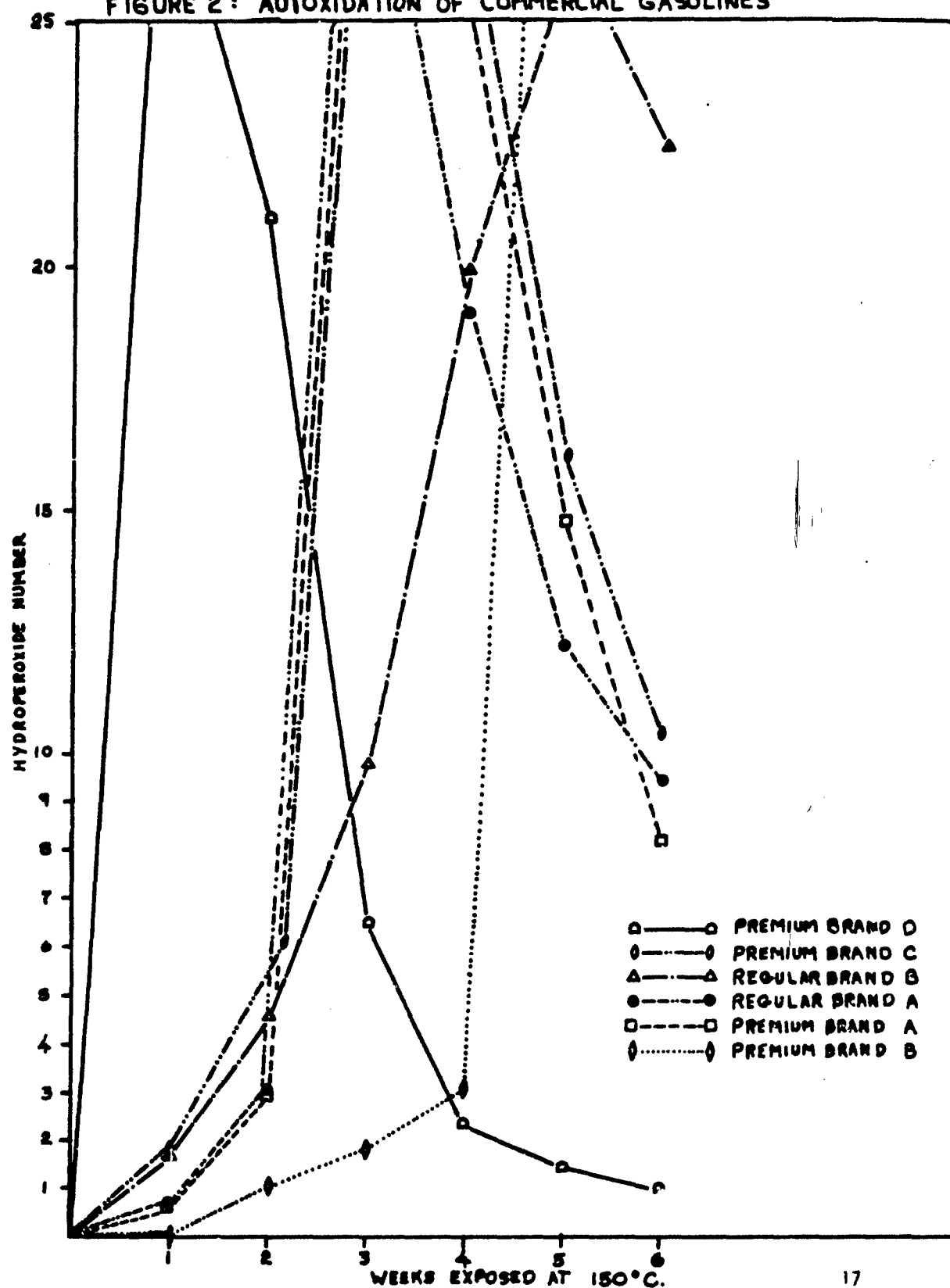


FIGURE 3: AUTOXIDATION OF MIL-G-3056B FROM BULK STORAGE

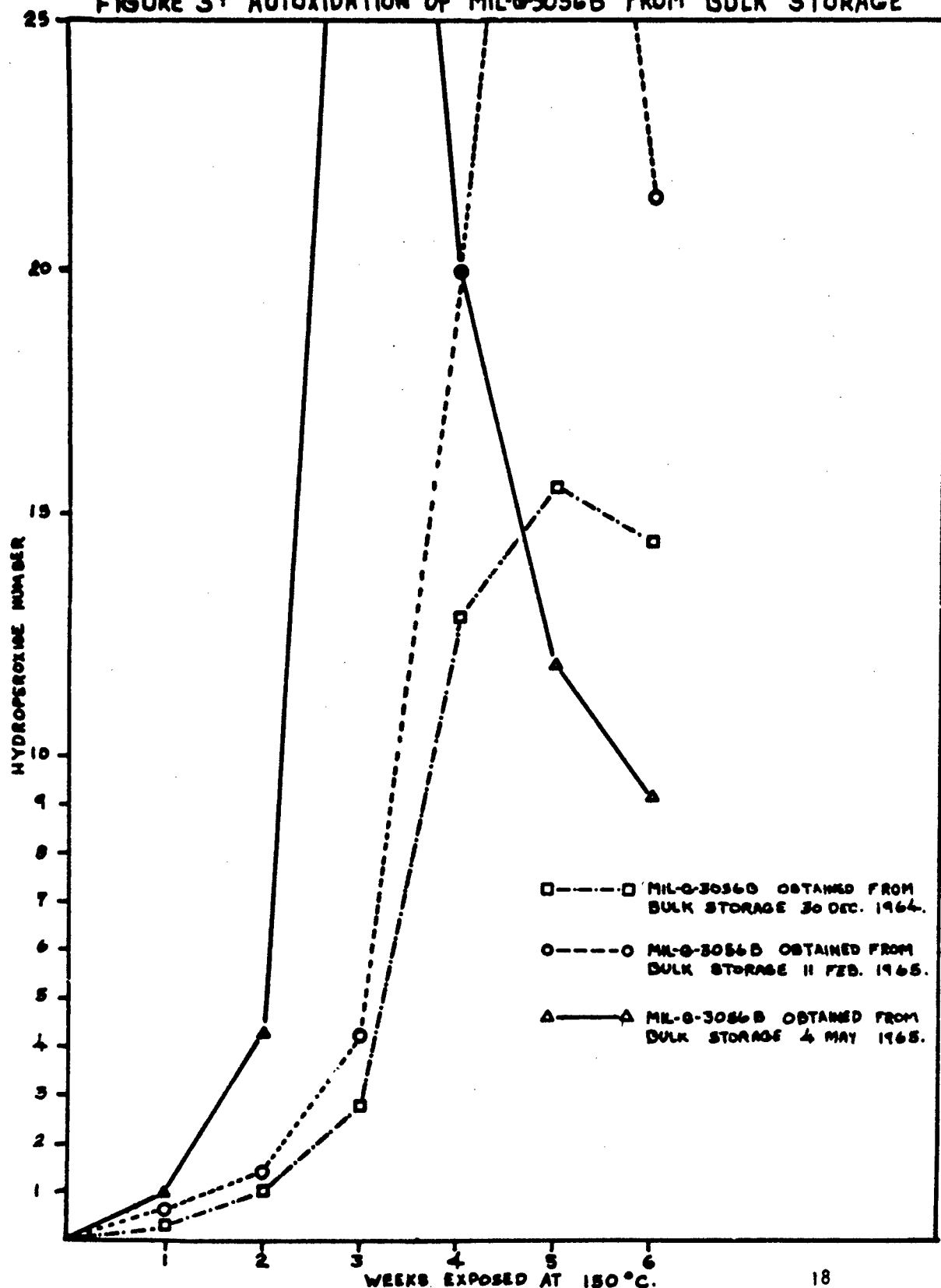
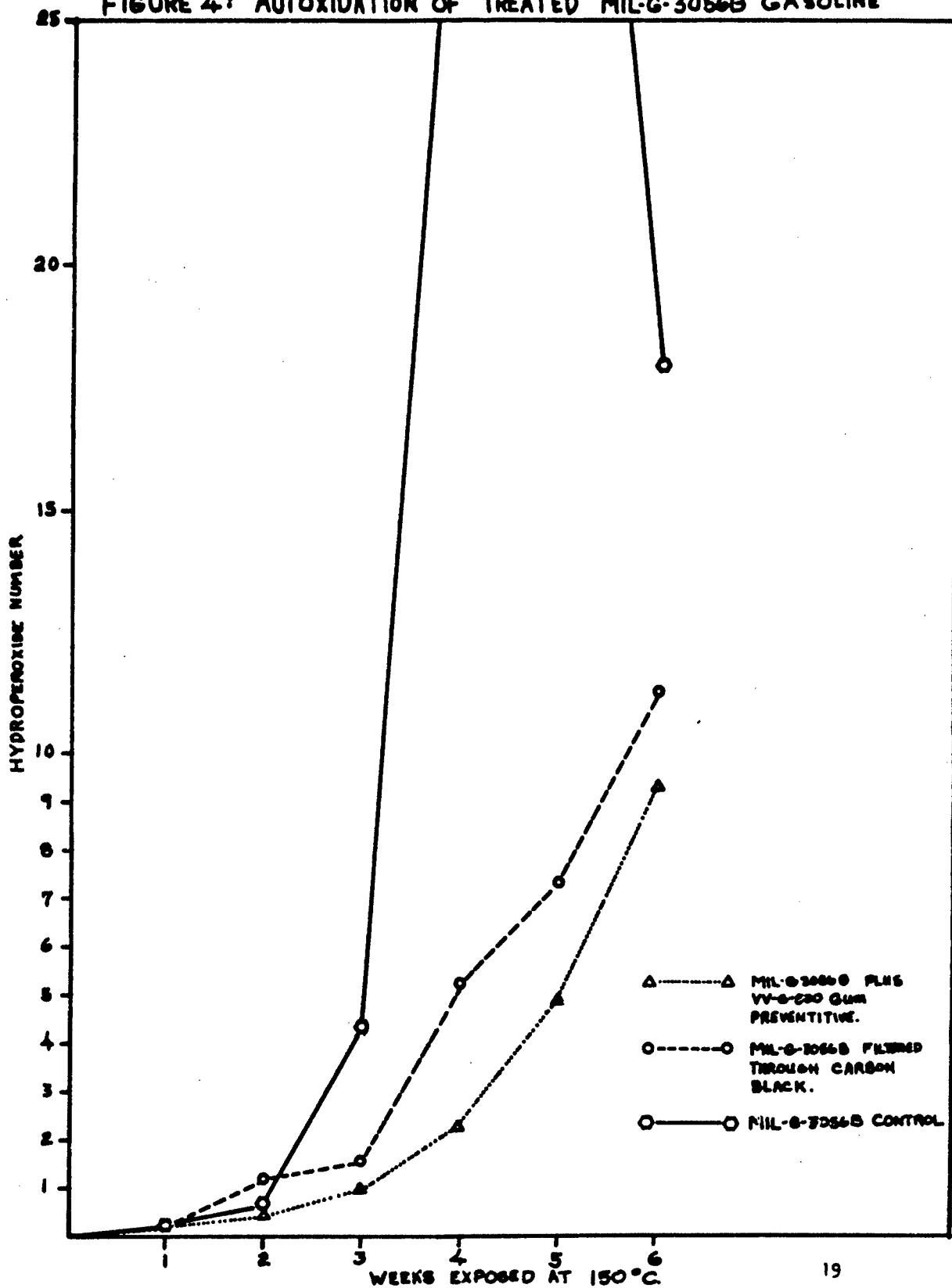


FIGURE 4: AUTOXIDATION OF 'TREATED' MIL-G-3056B GASOLINE



SUPPLEMENT FOR FIGURES 1 THROUGH 4

HYDROPEROXIDE VALUES FOR TEST FUELS EXPOSED AT 150°C.

Fuel Evaluated	Initial Value	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks
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For Figure 1:

VV-G-109, Gasoline Unleaded	0.07	19.11	49.89	69.68	54.17	42.20	33.73
MIL-G-30568, Gasoline Combat	0.00	0.35	1.00	2.81	12.85	15.74	14.92
VV-G-76, Gasoline Regular	0.12	0.35	0.73	1.05	2.44	2.86	10.19
MIL-J-5624F, Jet Fuel JP-4	0	0.15	0.18	0.20	0.20	0.10	0.15
MIL-F-45121, Fuel, C.I.T.E	0.10	0.40	0.45	0.35	0.35	0.25	0.22
MIL-G-5572C, Gasoline, Aviation	0	0	0	0.20	1.29	2.49	2.89

20

For Figure 2:

Premium Grade D	0.10	44.66	20.72	6.53	2.30	1.45	1.05
Premium Grade C	0.15	1.81	6.15	49.05	26.52	16.10	10.40
Regular Grade B	0.20	1.68	4.49	9.73	13.15	26.49	22.39
Regular Grade A	0.21	0.67	3.11	35.05	19.05	12.30	9.45
Premium Grade A	0.15	0.71	3.17	49.48	27.06	14.91	5.60
Premium Grade B	0.05	0.09	1.07	1.84	3.06	48.06	24.55

For Figure 3:

MIL-G-30568 (30 Dec. 1964)	0	0.35	1.00	2.81	12.85	15.74	4.92
MIL-G-30568 (11 Feb. 1965)	0.07	0.60	1.38	4.18	19.93	42.14	21.50
MIL-G-30568 (4 May 1965)	0.00	0.95	4.31	42.60	19.93	11.83	9.23

SUPPLEMENT FOR FIGURES 1 THROUGH 4
CONTINUED

HYDROPEROXIDE VALUES FOR TEST FUELS EXPOSED AT 150°C.

Fuel Evaluated	Initial Value	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks
For Figure 4:							
MIL-G-30568, Control	0.10	0.30	0.75	4.31	44.56	31.60	18.60
MIL-G-30568 (Carbon Black)	0.21	0.55	1.20	1.61	5.31	7.43	11.31
MIL-G-30568 (+VV-G-800)	0.00	0.25	0.40	0.99	2.30	4.95	9.31

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	ROLE	WT	ROLE	WT	ROLE	WT
Fuel instability Autoxidation Peroxide formation Deterioration Accelerated storage Free-radical chain reaction						

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